

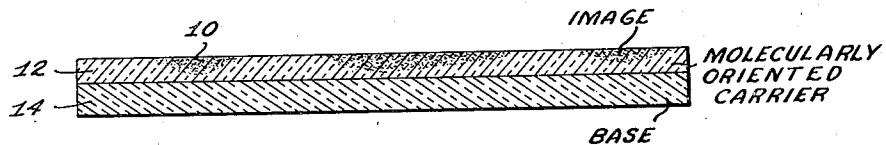
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PROCESS OF FORMING IODINE IMAGES

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## PROCESS OF FORMING IODINE IMAGES

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This invention relates to methods of forming images of materials, such as iodine, which plane polarize light when supported by, or suspended in, a suitable molecularly oriented plastic carrier, and to methods of producing said images in such carriers.

It is one object of the present invention to provide a novel method of producing images whose contrast is a function of the direction of vibration of incident light, which images are known as "vectographs" and, more specifically, to provide vectographs which are reproductions of photographic images.

Another object of the invention is to provide a novel method of so transforming an image produced by exposing and developing a photosensitive emulsion as to produce a corresponding image in a dichroic material.

It is a further object of the invention to provide a novel method of chemically transforming an image in silver to an image in iodine.

Further objects of the invention are the provision of a method of conventionally exposing and developing a silver halide emulsion and thereafter subjecting said emulsion to a plurality of novel chemical transformations whereby iodine replaces the exposed silver halide particles of the original emulsion; the provision of a novel method of effecting the desired chemical transformation from silver to iodine whereby the iodine image is substantially as sharply and as clearly defined in the carrier as the original silver image; the provision of a novel photosensitive emulsion comprising a silver halide in a molecularly oriented plastic carrier, which carrier when stained with iodine, is adapted to render said stain dichroic; the use of an oriented sheet of polyvinyl alcohol surfaced with a conventional silver halide emulsion, as for example, of gelatin, in carrying out the novel transformation of the invention to obtain a corresponding dichroic image; and the provision of a novel method of obtaining an iodine image in an unoriented material and of transferring said image to a molecularly oriented plastic carrier, as by a surface-to-surface contact, for the purpose of producing a corresponding dichroic image in said carrier.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention, accordingly, comprises the several steps and relation of one of said steps with respect to each of the others, which are exemplified in the following disclosure and the scope of the application of which will be indicated in the claims.

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This invention contemplates the production of a predetermined image, or the like, by the transformation of a portion of at least the surface area of a non-polarizing material to a polarizing surface, whereby said image is obtained in polarized light. In accordance with the invention an emulsion of a photosensitive material, such as a silver halide, is exposed and developed, as well understood in the art, to form an image in silver and is thereafter subjected to a novel chemical transformation whereby the silver image is converted into a corresponding iodine image.

There is illustrated by way of example in the drawing one form of sheet material for carrying out the method of the invention in which the silver image 10 is formed in an emulsion wherein the suspending agent for the silver particles consists of a sheet or layer 12 of oriented plastic, which plastic is of such character that iodine is adapted to produce therein a light-polarizing stain. In another form of the invention the oriented plastic sheet, instead of forming part of the photosensitive emulsion from which the silver image is obtained, may constitute a base or a support for a conventional silver halide emulsion, as for example of gelatin. In still another form of the invention the silver halide emulsion may comprise a suspension of the photosensitive material in a mixture of gelatin and polyvinyl alcohol. It is also to be understood that other transformations of silver to iodine are within the scope of the invention, as for example, a positive print in silver may have the silver image converted to an iodine image, in accordance with the processes of the invention, and the latter may then be imprinted by a suitable transfer process on a sheet of oriented plastic to produce in said sheet a dichroic image which will correspond to the silver image.

In the preferred embodiments of the present invention, the molecularly oriented carrier in which the dichroic image is formed is a sheet of transparent, high molecular weight polymer adapted to form a dichroic sorption complex with iodine, said polymer preferably containing hydroxyl groups, and examples of suitable polymers are polyvinyl alcohol, partially hydrolyzed polyvinyl acetals and polyvinyl alcohol esters, and regenerated cellulose. Of the materials falling within this class the preferred material is polyvinyl alcohol and images formed in properly prepared sheets of that material possess the highest dichroism and hence are more suitable in the production of dichroic images.

In order to obtain the best results with respect

to dichroism in the images of the present invention, at least the surface molecules of the plastic carrier should first be oriented to substantial parallelism. This may be conveniently accomplished by softening the sheet, as for example by subjecting to heat and then stretching or extending the sheet until suitable orientation of the molecules has been obtained. In the case of polyvinyl alcohol, a sheet formed by casting may be placed in satisfactory condition for the formation of dichroic images therein by subjecting the sheet to mechanical stress, as for example, by stretching in a uniform direction until the molecules therein are sufficiently oriented. A stretch of from two to six times the original length of the sheet produces good result. Alternatively, the surface molecules of a sheet of polyvinyl alcohol may be oriented, as by application of linear frictional force thereto, without orienting the molecules throughout the remainder of the sheet.

Where an image in polarized light is to be formed in a molecularly oriented plastic carrier by a chemical transformation of a silver image in said carrier to an iodine image, the plastic carrier is preferably one which maintains its orientation and is stable throughout the steps comprising the novel process of the invention and which is capable of supporting a dispersion of the photosensitive material from which the silver image is formed. Polyvinyl alcohol is a preferred material for the plastic carrier for the further reasons that it is stable in, and is permeable by, the solutions which convert and transform the silver halide to a silver image and the silver image to the ultimate dichroic stain of iodine. Polyvinyl alcohol is also relatively insoluble in said solutions so that a sharp dichroic image is obtained, despite the several transformations which constitute the novel process of the invention.

The plastic carrier in any of the processes comprehended by the present invention may be supported in a sheet 14 of a transparent plastic, as for example a cellulosic plastic, such as cellulose acetate and cellulose nitrate, or a vinyl compound, such as the vinyl acetals, vinyl acetate, vinyl chloride, the vinyl acetate-vinyl chloride copolymers, or a condensation type superpolymer, such as a polyamide or nylon type plastic. Cellulose acetate is a preferred material for the support and to form the most satisfactory material for the dichroic image there is bonded to at least one face of a sheet of said acetate, a sheet of molecularly oriented polyvinyl alcohol having a hydroxyl content, preferably in excess of 50%, said polyvinyl alcohol sheet being uniformly oriented throughout its entire thickness.

The following description of the invention is given by way of example in connection with a material having an oriented carrier provided with a silver image on only one surface thereof whereby a single image in polarized light is obtained in the final product. It is to be expressly understood, however, that the process is equally applicable to the formation of dichroic images on a material having both of its faces molecularly oriented and constituting part of, or supporting on, both of its oriented faces, silver suspensions providing desired images. The images may be of the same object and may bear a predetermined relation to one another. For example, one may be the left eye image and the other the right eye image of a stereoscopic pair and the directions of the molecular orientations of the plastic layers carrying said images may be at substantially right angles to one another so that an observer of the

iodine images formed from said silver images, provided with a pair of suitably oriented analyzers, may have only the left eye image rendered visible to his left eye and only the right eye image to his right eye, whereby the object is seen stereoscopically.

In one embodiment of the invention a silver halide emulsion in polyvinyl alcohol is exposed and developed by conventional photographic methods to produce an image in silver in the polyvinyl alcohol, and the silver image is thereafter transformed to a silver ferrocyanide image, which in turn is converted to an image formed of an oxidizing agent, the latter being adapted to release iodine from an iodide. The polyvinyl alcohol suspension of the oxidizing agent is then reacted in an iodide and a material adapted to dissolve said agent, thereby releasing iodine from the iodide. As a result of this transformation, the iodine is physically located at the same points on the exposed surface as the original exposed silver halide particles and forms the desired dichroic image in the polyvinyl alcohol.

To transform the silver to silver ferrocyanide, the suspension of silver in polyvinyl alcohol is bleached by a suitable ferricyanide, for example, potassium ferricyanide, sodium ferricyanide, or ammonium ferricyanide. The silver ferrocyanide thus obtained is then reacted with the salt of a polyvalent metal, which is in its higher valence form and which forms with the silver ferrocyanide a water-insoluble metallic ferrocyanide. Examples of suitable salts for this step are the cupric and ferric salts, such as cupric chloride, cupric sulfate, ferric chloride, ferric sulfate, and ferric ammonium sulfate. The silver salts which are in the emulsion at the completion of this reaction are preferably removed, as by washing in a relatively weak solution of sodium thiosulfate.

To produce the iodine image, the water-insoluble metallic ferrocyanide, which is the product of the last reaction, is transformed to its corresponding water-insoluble hydroxide by reaction with a suitable base, such as sodium or potassium hydroxide. The metallic hydroxide is then reacted with an iodide in the presence of an acid, as for example an acid solution of the iodide, to release iodine which replaces the hydroxide and forms the image in the polyvinyl alcohol. Examples of suitable iodides for this step are sodium iodide, potassium iodide and ammonium iodide, and these may be used in solution with any of a large number of acids, of which hydrochloric, sulphuric and maleic acids are preferred examples.

In the above process the transformation of silver to silver ferrocyanide and the conversion of the silver ferrocyanide to the ferrocyanide salt of a polyvalent metal in its high valence form, have been described as two distinct operations and may be carried out in separate solutions. However, the conversion of silver to the metallic ferrocyanide may be carried out more rapidly by effecting the transformation in a single solution containing both reactants, i. e., the ferricyanide and the metallic salt. If the reactions are carried out in this preferred manner, i. e., in a single solution, precautions are taken to prevent direct reaction of the metallic salt and the ferricyanide. This may be accomplished by the addition to the solution of a suitable composition comprising an organic salt, such as ammonium oxalate, and an acid, such as oxalic acid, the latter acting also as an accelerator. Other materials which may be used instead of ammonium oxalate for preventing undesired interaction between the components of

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the solution are, for example, potassium oxalate, potassium citrate, ammonium citrate, potassium-sodium tartrate, ammonium tartrate, sodium succinate and other organic salts. Instead of oxalic acid, other acids, such as hydrochloric acid and weak alkalies, for example, sodium carbonate, potassium carbonate and ammonium carbonate, may be used.

It will now be apparent to those skilled in the art that the above method of transforming a silver image to an iodine image will render unnecessary the stopping and fixing of the silver image produced by developing the exposed silver halide-polyvinyl alcohol emulsion, so that one or both of these operations may be eliminated. It is preferable, however, to perform at least the stopping by conventional methods. The entire operation after the stopping can be carried out in daylight, without affecting the quality of the final product. It is preferable also to wash the print after each operation which follows the removal of the silver salts from the emulsion.

The above process can be readily adapted for transforming the silver image of a conventional photographic paper print to an iodine image, which iodine image can then be transferred to a sheet comprising at least a surface layer of molecularly oriented polyvinyl alcohol. In a preferred adaptation of the transfer process, the iodine is not released until the paper print is brought into intimate contact with the polyvinyl alcohol surface. This modification of the process comprises transforming the silver image in the paper print to a hydroxide of a polyvalent metal in its higher valence form, as described above, and then immersing the print in a solution of an iodide which does not contain an acid. This brings the iodide into intimate contact with the hydroxide image but because of the absence of the acid does not release iodine. The acid for rendering the metallic hydroxide capable of effecting the release of the free iodine from the iodide solution is contained in the oriented polyvinyl alcohol surface with which the print is then brought into surface contact. The iodine is thus simultaneously released and transferred to the polyvinyl alcohol surface. The acid, as for example maleic acid, may be introduced into the polyvinyl alcohol surface in any well known manner, as by casting the polyvinyl alcohol layer or sheet with the acid contained in the casting solution. Where this transfer method of obtaining dichroic images is used, it is unnecessary to wash out the silver salts after the metallic ferrocyanide image is formed.

An alternative method of transforming a silver image to an iodine image, in accordance with the present invention, is to react the silver with a solution of a permanganate, as for example potassium or sodium permanganate, to form an image comprising the relatively insoluble manganese dioxide. The latter serves to release iodine from an acid solution of an iodide in much the same manner as the ferric hydroxide in the foregoing examples releases iodine.

Still another method is to react the silver image with a solution containing a bichromate, such as potassium or sodium bichromate, and a metallic salt, such as lead nitrate, which will form as a product of the reaction an insoluble metal chromate. The reaction, when lead nitrate is used, gives an image comprising lead chromate which acts in an acid solution of iodide to release iodine. A modification of this method is the use of a bichromate without the metallic salt, in

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which event the image is formed in silver chromate, which is also insoluble in water and acts as an oxidizing agent. However, in the last-named modification of the process, because the insoluble image is formed of a silver salt, the release of iodine is accompanied by the formation of an insoluble secondary image. Accordingly, said method is useful primarily in connection with methods wherein the iodine image after formation, or as it is formed, is transferred to a molecularly oriented plastic sheet.

It is to be understood that the invention comprehends any process wherein a silver image is transformed or converted by suitable reaction to an image comprising a compound which releases iodine from an iodide in a solution containing a solvent for said compound, such for example, as an acid.

The following examples of the novel processes of the present invention are given for purposes of illustration, but it is to be expressly understood that the proportions may be varied within wide ranges and that the ingredients may also be varied as specified hereinabove and as will now be apparent to those skilled in the art.

#### Example 1

A layer or sheet of molecularly oriented polyvinyl alcohol containing, or supporting, a silver halide emulsion and mounted on a suitable supporting sheet of cellulose acetate, is exposed, developed, and stopped, in accordance with conventional photographic methods. It is preferably washed in water and is then immersed in a bath consisting of:

|                                                      |       |
|------------------------------------------------------|-------|
|                                                      | c. c. |
| Ammonium oxalate, saturated solution.....            | 100   |
| Cupric sulfate, ten per cent solution.....           | 20    |
| Potassium ferriocyanide, ten per cent solution ..... | 15    |
| Oxalic acid, saturated solution.....                 | 5     |

The bath is preferably prepared by mixing the ingredients in the order in which they are named and is maintained at approximately room temperature. The time required for this step of the process is not critical since reactions to completion are involved, immersion for two minutes or more giving good results.

The print is then washed in a 5% sodium thiosulfate solution to remove the silver salts, and then with water. It is immersed in a 1.5% solution of sodium hydroxide for several seconds and is then washed in water and placed in an acid solution of potassium iodide comprising:

|                                              |       |
|----------------------------------------------|-------|
|                                              | c. c. |
| Potassium iodide, ten per cent solution..... | 100   |
| Hydrochloric acid, N solution.....           | 20    |

The product of this immersion contains an image in iodine. It is preferable to immerse the print in a final fixing bath, which bath contains boric acid to stabilize the dichroic image. The fixing bath may also contain sodium sulfate to prevent softening of the sheet; potassium iodide to provide a control for the color of the image and in some instances a weak solution of sodium thiosulfate.

#### Example 2

The process is carried out in the same manner and with the same materials as that of Example 1, except that the silver image is transformed to

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a ferric ferrocyanide instead of a cupric ferrocyanide image by a solution consisting of:

|                                                    |       |
|----------------------------------------------------|-------|
|                                                    | c. c. |
| Iron alum, ten per cent solution.....              | 5.0   |
| Potassium ferricyanide, ten per cent solution..... | 4     |
| Oxalic acid, saturated solution.....               | 12    |
| Ammonium alum, saturated solution.....             | 20    |
| Hydrochloric acid, N solution.....                 | 3.0   |
| Water.....                                         | 180   |

and the iodine is released in a solution of potassium iodide comprising:

|                                              |       |
|----------------------------------------------|-------|
|                                              | c. c. |
| Potassium iodide, ten per cent solution..... | 100   |
| Hydrochloric acid, N solution.....           | 30    |

### Example 3

A conventional paper print having a silver image formed thereon is immersed in either of the aforementioned solutions for obtaining the metallic ferrocyanide image, an immersion in either of said solutions for over two minutes giving good results. It is then immersed in the sodium hydroxide bath either with or without being first washed in sodium thiosulfate to remove the silver salts. The print is then dipped in a 10% potassium iodide solution which contains no acid. Thereafter, a sheet comprising an outer layer of molecularly oriented polyvinyl alcohol, containing approximately 10% by weight of maleic acid, is brought into contact with said print whereby iodide is released and is transferred to said sheet to give the desired dichroic image.

### Example 4

A conventional paper print having a silver image formed thereon is immersed in a bleaching solution consisting of:

|                                                  |       |
|--------------------------------------------------|-------|
|                                                  | c. c. |
| Potassium dichromate, one per cent solution..... | 100   |
| Hydrochloric acid, N solution.....               | 5     |

for approximately one minute, and is then washed and cleared in a 1% solution of sodium bicarbonate, a washing for about one minute in the latter solution being sufficient. The print is then washed thoroughly and dipped into a 10% neutral solution of potassium iodide. Thereafter, a sheet comprising an outer layer of molecularly oriented polyvinyl alcohol, containing approximately 10% by weight of maleic acid, is brought into contact with said print whereby iodine is released and is transferred to said sheet to give the desired dichroic image.

### Example 5

A paper print containing a silver image is immersed in a bleaching solution consisting of a mixture of a solution of:

|                             |     |
|-----------------------------|-----|
| Lead nitrate.....grams..... | 7   |
| Water.....c. c.....         | 100 |

and a solution of:

|                                       |     |
|---------------------------------------|-----|
| Potassium ferricyanide.....grams..... | 4   |
| Glacial acetic acid.....c. c.....     | 2   |
| Water.....c. c.....                   | 300 |

and is bleached therein for approximately five minutes. The print is then immersed in a solution consisting of:

|                                    |     |
|------------------------------------|-----|
| Potassium dichromate.....gram..... | 1   |
| Water.....c. c.....                | 200 |

for approximately three minutes. It is preferably washed and then cleared, for example, in a

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1% solution of nitric acid, by immersion in said acid for approximately two minutes. The print may be washed again and is then dipped in a neutral 10% potassium iodide solution. Thereafter, a sheet comprising an outer layer of molecularly oriented polyvinyl alcohol, containing approximately 10% by weight of maleic acid, is brought into contact with said print whereby iodine is released and is transferred to said sheet to give the desired dichroic image.

### Example 6

A paper print is immersed for about two minutes in a bleaching solution consisting of:

|                                                     |       |
|-----------------------------------------------------|-------|
|                                                     | c. c. |
| Potassium permanganate, five per cent solution..... | 6     |
| Water.....                                          | 200   |

and is thereafter washed thoroughly. It may be cleared in a 2% hydrochloric acid solution and is then dipped in a neutral 10% potassium iodide solution. Thereafter, a sheet comprising an outer layer of molecularly oriented polyvinyl alcohol, containing approximately 10% by weight of maleic acid, is brought into contact with said print whereby iodine is released and is transferred to said sheet to give the desired dichroic image.

It will be noted that in every example given above, it is contemplated that the iodine image will be formed in a sheet of a high polymer which is molecularly oriented. It is conceivable that the novel transformation of a silver image to an iodine image may be useful in connection with other processes than the formation of dichroic images and, accordingly, it is expressly understood that unless the claims so specify, they are not limited to the formation of an iodine image in a carrier which is molecularly oriented. Where an oriented carrier is used, i. e., a dichroic image is desired, it is preferable that all those portions of the carrier penetrated by the iodine be molecularly oriented since application of the dichroic material to unoriented portions will produce a non-dichroic light-absorbing stain.

As has been previously stated, the foregoing description is illustrative only of operative embodiments of the present invention. It must be emphasized that each step therein is a variable, and that none of the ingredients, times, or proportions for any step or solution are critical except insofar as they may be made so by the other variables. The specific examples given comprise operative embodiments of the invention with which excellent results have been obtained. However, considerable variation is possible in virtually any degree thereof, and one or more solutions or steps can be compensated for in the other steps. It is, accordingly, obvious that no set rules can be given and it would be difficult, if not impossible, even to set outside limits on the range of variation.

It should be pointed out also that although the foregoing description emphasizes the formation of iodine images which are duplicates of photographic silver images, the invention is in no way limited to the exclusive use of photographically obtained silver images.

It is to be understood that the term "relatively water-insoluble" as utilized in the claims in reference to the carrier for the silver image refers to an insolubility such as will prevent water solutions from appreciably dissolving said carrier in the time in which the reactions transforming the silver image to the iodine image take place.

It is also to be understood that the term "image in iodine" as used in the claims refers to an image formed of iodine or its complexes.

Since certain changes may be made in carrying out the above process without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all the generic and specific features of the invention herein described, and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

What is claimed is:

1. The method of producing an iodine image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image formed of a relatively water-insoluble oxidizing agent, and reacting said last-named image with an iodide in the presence of a solvent for said water-insoluble oxidizing agent which dissolves the latter and causes it to release iodine from the iodide whereby the iodine which is released replaces the oxidizing agent to form an image in iodine.

2. The method of producing an iodine image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image formed of a relatively water-insoluble oxidizing compound of a polyvalent metal in a higher valence form, and reacting said last-named image with an iodide in the presence of a solvent for said water-insoluble oxidizing compound which dissolves the latter and causes it to release iodine from the iodide whereby the iodine which is released replaces the oxidizing compound to form an image in iodine.

3. The method of producing an iodine image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image comprising a relatively water-insoluble hydroxide of a polyvalent metal in a higher valence form, and reacting said last-named image with an iodide in the presence of a solvent for said hydroxide which dissolves the latter and causes it to release iodine from the iodide whereby the iodine which is released replaces the hydroxide to form an image in iodine.

4. The method of producing an iodine image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image comprising a relatively water-insoluble chromate, and reacting said last-named image with an iodide in the presence of a solvent for said chromate which dissolves the latter and causes it to release iodine from the iodide whereby the iodine which is released replaces the chromate to form an image in iodine.

5. The method of producing an iodine image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image formed of a relatively water-insoluble oxidizing agent, and reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the oxidizing agent to form an image in iodine.

6. The method of producing an iodine image, which comprises forming the image in silver in

a permeable, relatively water-insoluble carrier, transforming said silver image to an image formed of a relatively water-insoluble oxidizing compound of a polyvalent metal in a higher valence form, and reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the oxidizing compound to form an image in iodine.

7. The method of producing an iodine image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image comprising a relatively water-insoluble hydroxide of a polyvalent metal in a higher valence form, and reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the hydroxide to form an image in iodine.

8. The method of producing an iodine image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image comprising cupric hydroxide, and reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the hydroxide to form an image in iodine.

9. The method of producing an iodine image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image comprising ferric hydroxide, and reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the hydroxide to form an image in iodine.

10. The method of producing an iodine image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image comprising a relatively water-insoluble chromate of a metal by reacting said silver image with a bichromate and a salt of said metal, and reacting said chromate image with an iodide in the presence of an acid whereby iodine is released and replaces the chromate to form an image in iodine.

11. The method of producing an iodine image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, reacting said silver image with a ferricyanide to form an image comprising silver ferrocyanide, reacting said ferrocyanide image with a salt of a polyvalent metal in a higher valence form to transform the image to an image comprising a water-insoluble ferrocyanide of said metal, transforming said last-named image to an image comprising the hydroxide of said metal, and reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the hydroxide to form an image in iodine.

12. The method of producing an iodine image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image comprising ferric ferrocyanide by reacting said silver image with a ferricyanide and then reacting the product of said reaction with a ferric salt, transforming the ferric ferrocyanide image to an image comprising ferric hydroxide by reaction with a base, and reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the ferric hydroxide to form an image in iodine.

13. The method of producing an iodine image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image com-

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prising cupric ferrocyanide by reacting said silver image with a ferricyanide and then reacting the product of said reaction with a cupric salt, transforming the cupric ferrocyanide image to an image comprising cupric hydroxide by reaction with a base, and reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the cupric hydroxide to form an image in iodine.

14. The method of producing an iodine image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image comprising a water-insoluble ferrocyanide of a polyvalent metal in a higher valence form by immersing said carrier in a solution comprising a ferricyanide, a salt of said metal and an organic compound adapted to inhibit direct reaction between said ferricyanide and said salt, transforming said metal ferrocyanide image to an image comprising a hydroxide of said metal, and reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the metal hydroxide to form an image in iodine.

15. The method of producing a dichroic image, which comprises forming the image in silver in a relatively water-insoluble carrier comprising at least a layer of a permeable molecularly oriented high polymer having an affinity for iodine and adapted to form a dichroic sorption complex therewith, said layer supporting said silver image, transforming said silver image to an image formed of a relatively water-insoluble oxidizing agent, and reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the oxidizing agent to form an image in iodine.

16. The method of producing a dichroic image, which comprises forming the image in silver in a relatively water-insoluble carrier comprising at least a layer of a permeable molecularly oriented high polymer having an affinity for iodine and adapted to form a dichroic sorption complex therewith, said layer supporting said silver image, transforming said silver image to an image formed of a relatively water-insoluble oxidizing compound of a polyvalent metal in a higher valence form, and reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the oxidizing compound to form an image in iodine.

17. The method of producing a dichroic image, which comprises forming the image in silver in a relatively water-insoluble carrier comprising at least a layer of a permeable molecularly oriented high polymer having an affinity for iodine and adapted to form a dichroic sorption complex therewith, said layer supporting said silver image, transforming said silver image to an image comprising a relatively water-insoluble hydroxide of a polyvalent metal in a higher valence form, and reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the hydroxide to form an image in iodine.

18. The method of producing a dichroic image, which comprises forming the image in silver in a relatively water-insoluble carrier comprising at least a layer of a permeable molecularly oriented high polymer having an affinity for iodine and adapted to form a dichroic sorption complex therewith, said layer supporting said silver image, transforming said silver image to an image comprising cupric hydroxide, and re-

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acting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the hydroxide to form an image in iodine.

19. The method of producing a dichroic image, which comprises forming the image in silver in a relatively water-insoluble carrier comprising at least a layer of a permeable molecularly oriented high polymer having an affinity for iodine and adapted to form a dichroic sorption complex therewith, said layer supporting said silver image, transforming said silver image to an image comprising ferric hydroxide, and reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the hydroxide to form an image in iodine.

20. The method of producing a dichroic image, which comprises forming the image in silver in a relatively water-insoluble carrier comprising at least a layer of a permeable molecularly oriented high polymer having an affinity for iodine and adapted to form a dichroic sorption complex therewith, said layer supporting said silver image, transforming said silver image to an image comprising a relatively water-insoluble chromate, and reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the chromate to form an image in iodine.

21. The method of producing a dichroic image, which comprises forming the image in silver in a relatively water-insoluble carrier comprising at least a layer of a permeable molecularly oriented high polymer having an affinity for iodine and adapted to form a dichroic sorption complex therewith, said layer supporting said silver image, reacting said silver image with a ferricyanide to form an image comprising silver ferrocyanide, reacting said ferrocyanide image with a salt of a polyvalent metal in a higher valence form to transform the image to an image comprising a water-insoluble ferrocyanide of said metal, transforming said last-named image to an image comprising the hydroxide of said metal, and reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the hydroxide to form an image in iodine.

22. The method of producing a dichroic image, which comprises forming the image in silver in a relatively water-insoluble carrier comprising at least a layer of a permeable molecularly oriented high polymer having an affinity for iodine and adapted to form a dichroic sorption complex therewith, said layer supporting said silver image, transforming said silver image to an image comprising ferric ferrocyanide by reacting said silver image with a ferricyanide and then reacting the product of said reaction with ferric salt, transforming the ferric ferrocyanide image to an image comprising ferric hydroxide by reaction with a base, and reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the ferric hydroxide to form an image in iodine.

23. The method of producing a dichroic image, which comprises forming the image in silver in a relatively water-insoluble carrier comprising at least a layer of a permeable molecularly oriented high polymer having an affinity for iodine and adapted to form a dichroic sorption complex therewith, said layer supporting said silver image, transforming said silver image to an image comprising cupric ferrocyanide by reacting said sil-

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ver image with a ferricyanide and then reacting the product of said reaction with a cupric salt, transforming the cupric ferrocyanide image to an image comprising cupric hydroxide by reaction with a base, and reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the cupric hydroxide to form an image in iodine.

24. The method of producing a dichroic image, which comprises forming the image in silver in a carrier having at least the layer which supports said silver formed of a molecularly oriented polyvinyl alcohol, transforming said silver image to an image formed of a relatively water-insoluble oxidizing compound of a polyvalent metal in a higher valence form, and reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the oxidizing compound to form an image in iodine.

25. The method of producing a dichroic image, which comprises forming the image in silver in a carrier having at least the layer which supports said silver formed of a molecularly oriented polyvinyl alcohol, transforming said silver image to an image comprising a relatively water-insoluble hydroxide of a polyvalent metal in a higher valence form, and reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the hydroxide to form an image in iodine.

26. The method of producing a dichroic image, which comprises forming the image in silver in a carrier having at least the layer which supports said silver formed of a molecularly oriented polyvinyl alcohol, reacting said silver image with a ferricyanide to form an image comprising silver ferrocyanide, reacting said ferrocyanide image with a salt of a polyvalent metal in a higher valence form to transform the image to an image comprising a water-soluble ferrocyanide of said metal, transforming said last-named image to an image comprising the hydroxide of said metal, and reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the hydroxide to form an image in iodine.

27. The method of producing a dichroic image, which comprises forming the image in silver in a carrier having at least the layer which supports said silver formed of a molecularly oriented polyvinyl alcohol, transforming said silver image to an image comprising ferric ferrocyanide by reacting said silver image with a ferricyanide and then reacting the product of said reaction with a ferric salt, transforming the ferric ferrocyanide image to an image comprising ferric hydroxide by reaction with a base, and reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the ferric hydroxide to form an image in iodine.

28. The method of producing a dichroic image, which comprises forming the image in silver in a carrier having at least the layer which supports said silver formed of a molecularly oriented polyvinyl alcohol, transforming said silver image to an image comprising cupric ferrocyanide by reacting said silver image with a ferricyanide and then reacting the product of said reaction with a cupric salt, transforming the cupric ferrocyanide image to an image comprising cupric hydroxide by reaction with a base, and reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and re-

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places the cupric hydroxide to form an image in iodine.

29. The method of producing a dichroic image, which comprises forming the image in silver in a carrier having at least the layer which supports said silver formed of a molecularly oriented polyvinyl alcohol, transforming said silver image to an image comprising a water-insoluble ferrocyanide of a polyvalent metal in a higher valence form by immersing said carrier in a solution comprising a ferricyanide, a salt of said metal and an organic compound adapted to inhibit direct reaction between said ferricyanide and said salt, transforming said metal ferrocyanide image to an image comprising a hydroxide of said metal, and reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the metal hydroxide to form an image in iodine.

30. The method of producing a dichroic image, which comprises forming the image in silver in a carrier having at least the layer which supports said silver formed of a molecularly oriented polyvinyl alcohol, transforming said silver image to an image comprising a relatively water-insoluble chromate of a metal by reacting said silver image with a bichromate and a salt of said metal, and reacting said chromate image with an iodide in the presence of an acid whereby iodine is released and replaces the chromate to form an image in iodine.

31. The method of producing a dichroic image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image formed of a relatively water-insoluble oxidizing agent, reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the oxidizing agent to form an image in iodine, and bringing into face-to-face contact with said carrier a transparent molecularly oriented high polymer adapted to form a dichroic sorption complex with iodine and having a greater affinity for iodine than said carrier.

32. The method of producing a dichroic image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image formed of a relatively water-insoluble oxidizing compound of a polyvalent metal in a higher valence form, reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the oxidizing compound to form an image in iodine, and bringing into face-to-face contact with said carrier a transparent molecularly oriented high polymer adapted to form a dichroic sorption complex with iodine and having a greater affinity for iodine than said carrier.

33. The method of producing a dichroic image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, reacting said silver image with a ferricyanide to form an image comprising silver ferrocyanide, reacting said ferrocyanide image with a salt of a polyvalent metal in a higher valence form to transform the image to an image comprising a water-insoluble ferrocyanide of said metal, transforming said last-named image to an image comprising the hydroxide of said metal, reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the hydroxide to form an image in iodine, and bringing into face-to-face contact with said carrier a transparent molecularly oriented high polymer adapted to form a dichroic sorption com-

plex with iodine and having a greater affinity for iodine than said carrier.

34. The method of producing a dichroic image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image comprising ferric ferrocyanide by reacting said silver image with a ferricyanide and then reacting the product of said reaction with a ferric salt, transforming the ferric ferrocyanide image to an image comprising ferric hydroxide by reaction with a base, reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the ferric hydroxide to form an image in iodine, and bringing into face-to-face contact with said carrier a transparent molecularly oriented high polymer adapted to form a dichroic sorption complex with iodine and having a greater affinity for iodine than said carrier.

35. The method of producing a dichroic image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image comprising cupric ferrocyanide by reacting said silver image with a ferricyanide and then reacting the product of said reaction with a cupric salt, transforming the cupric ferrocyanide image to an image comprising cupric hydroxide by reaction with a base, reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the cupric hydroxide to form an image in iodine, and bringing into face-to-face contact with said carrier a transparent molecularly oriented high polymer adapted to form a dichroic sorption complex with iodine and having a greater affinity for iodine than said carrier.

36. The method of producing a dichroic image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image formed of a relatively water-insoluble oxidizing agent, reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the oxidizing agent to form an image in iodine, and bringing into face-to-face contact with said carrier a molecularly oriented polyvinyl alcohol.

37. The method of producing a dichroic image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image formed of a relatively water-insoluble oxidizing compound of a polyvalent metal in a higher valence form, reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the oxidizing compound to form an image in iodine, and bringing into face-to-face contact with said carrier a molecularly oriented polyvinyl alcohol.

38. The method of producing a dichroic image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, reacting said silver image with a ferricyanide to form an image comprising silver ferrocyanide, reacting said ferrocyanide image with a salt of a polyvalent metal in a higher valence form to transform the image to an image comprising a water-insoluble ferrocyanide of said metal, transforming said last-named image to an image comprising the hydroxide of said metal, reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the hydroxide to form an image in iodine,

and bringing into face-to-face contact with said carrier a molecularly oriented polyvinyl alcohol.

39. The method of producing a dichroic image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image comprising ferric ferrocyanide by reacting said silver image with a ferricyanide and then reacting the product of said reaction with a ferric salt, transforming the ferric ferrocyanide image to an image comprising ferric hydroxide by reaction with a base, reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the ferric hydroxide to form an image in iodine, and bringing into face-to-face contact with said carrier a molecularly oriented polyvinyl alcohol.

40. The method of producing a dichroic image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image comprising cupric ferrocyanide by reacting said silver image with a ferricyanide and then reacting the product of said reaction with a cupric salt, transforming the cupric ferrocyanide image to an image comprising cupric hydroxide by reaction with a base, reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the cupric hydroxide to form an image in iodine, and bringing into face-to-face contact with said carrier a molecularly oriented polyvinyl alcohol.

41. The method of producing a dichroic image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image formed of a relatively water-insoluble oxidizing agent, immersing said carrier in an iodide solution, and bringing said carrier into face-to-face contact with a transparent molecularly oriented high polymer containing an acid and adapted to form a dichroic sorption complex with iodine whereby iodine is released to produce an image in said polymer.

42. The method of producing a dichroic image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image formed of a relatively water-insoluble oxidizing compound of a polyvalent metal in a higher valence form, immersing said carrier in an iodide solution, and bringing said carrier into face-to-face contact with a transparent molecularly oriented high polymer containing an acid and adapted to form a dichroic sorption complex with iodine whereby iodine is released to produce an image in said polymer.

43. The method of producing a dichroic image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, reacting said silver image with a ferricyanide to form an image comprising silver ferrocyanide, reacting said ferrocyanide image with a salt of a polyvalent metal in a higher valence form to transform the image to an image comprising a water-insoluble ferrocyanide of said metal, transforming said last-named image to an image comprising the hydroxide of said metal, immersing said carrier in an iodide solution, and bringing said carrier into face-to-face contact with a transparent molecularly oriented high polymer containing an acid and adapted to form a dichroic sorption complex with iodine whereby iodine is released to produce an image in said polymer.

44. The method of producing a dichroic image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image comprising ferric ferrocyanide by reacting said silver image with a ferricyanide and then reacting the product of said reaction with a ferric salt, transforming the ferric ferrocyanide image to an image comprising ferric hydroxide by reaction with a base, immersing said carrier in an iodide solution, and bringing said carrier into face-to-face contact with a transparent molecularly oriented high polymer containing an acid and adapted to form a dichroic sorption complex with iodine whereby iodine is released to produce an image in said polymer.

45. The method of producing a dichroic image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image comprising cupric ferrocyanide by reacting said silver image with a ferricyanide and then reacting the product of said reaction with a cupric salt, transforming the cupric ferrocyanide image to an image comprising cupric hydroxide by reaction with a base, immersing said carrier in an iodide solution, and bringing said carrier into face-to-face contact with a transparent molecularly oriented high polymer containing an acid and adapted to form a dichroic sorption complex with iodine whereby iodine is released to produce an image in said polymer.

46. The method of producing a dichroic image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image formed of a relatively water-insoluble oxidizing agent, immersing said carrier in an iodide solution, and bringing said carrier into face-to-face contact with a molecularly oriented polyvinyl alcohol containing an acid whereby iodine is released to provide an iodine image in said polyvinyl alcohol.

47. The method of producing a dichroic image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image formed of a relatively water-insoluble oxidizing compound of a polyvalent metal in a higher valence form, immersing said carrier in an iodide solution, and bringing said carrier into face-to-face contact with a molecularly oriented polyvinyl alcohol containing an acid whereby iodine is released to provide an iodine image in said polyvinyl alcohol.

48. The method of producing a dichroic image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, reacting said silver image with a ferricyanide to form an image comprising silver ferrocyanide, reacting said ferrocyanide image with a salt of a polyvalent metal in a higher valence form to transform the image to an image comprising a water-insoluble ferrocyanide of said metal, transforming said last-named image to an image comprising the hydroxide of said metal, immersing said carrier in an iodide solution, and bringing said carrier into face-to-face contact with a molecularly oriented polyvinyl alcohol containing an acid whereby iodine is released to provide an iodine image in said polyvinyl alcohol.

49. The method of producing a dichroic image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image com-

prising ferric ferrocyanide by reacting said silver image with a ferricyanide and then reacting the product of said reaction with a ferric salt, transforming the ferric ferrocyanide image to an image comprising ferric hydroxide by reaction with a hydroxide, immersing said carrier in an iodide solution, and bringing said carrier into face-to-face contact with a molecularly oriented polyvinyl alcohol containing an acid whereby iodine is released to provide an iodine image in said polyvinyl alcohol.

50. The method of producing a dichroic image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image comprising cupric ferrocyanide by reacting said silver image with a ferricyanide and then reacting the product of said reaction with a cupric salt, transforming the cupric ferrocyanide image to an image comprising cupric hydroxide by reaction with a hydroxide, immersing said carrier in an iodide solution, and bringing said carrier into face-to-face contact with a molecularly oriented polyvinyl alcohol containing an acid whereby iodine is released to provide an iodine image in said polyvinyl alcohol.

51. The method of producing a dichroic image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image comprising a relatively water-insoluble chromate, reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the chromate to form an image in iodine, and bringing into face-to-face contact with said carrier a transparent, molecularly oriented high polymer adapted to form a dichroic sorption complex with iodine and having a greater affinity for iodine than said carrier.

52. The method of producing a dichroic image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image comprising a relatively water-insoluble chromate, reacting said last-named image with an iodide in the presence of an acid whereby iodine is released and replaces the chromate to form an image in iodine, and bringing into face-to-face contact with said carrier a molecularly oriented polyvinyl alcohol.

53. The method of producing a dichroic image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image comprising a relatively water-insoluble chromate, immersing said carrier in an iodide, and bringing said carrier into face-to-face contact with a transparent, molecularly oriented high polymer containing an acid and adapted to form a dichroic sorption complex with iodine whereby iodine is released to produce an image in said polymer.

54. The method of producing a dichroic image, which comprises forming the image in silver in a permeable, relatively water-insoluble carrier, transforming said silver image to an image comprising a relatively water-insoluble chromate, immersing said carrier in an iodide, and bringing said carrier into face-to-face contact with a molecularly oriented polyvinyl alcohol containing an acid whereby iodine is released to provide an iodine image in said polyvinyl alcohol.

ARTHUR BARNES.  
HELEN P. HUSEK.

**Certificate of Correction**

Patent No. 2,409,923.

October 22, 1946.

ARTHUR BARNES ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Column 3, line 42, for "in a sheet" read *on a sheet*; column 7, line 33, for "iodide" read *iodine*; column 8, line 62, for "range" read *ranges*; column 12, line 60, claim 22, before "ferric" insert the article *a*; column 13, line 41, claim 26, for "water-soluble" read *water-insoluble*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 2nd day of November, A. D. 1948.

[SEAL]

THOMAS F. MURPHY,  
*Assistant Commissioner of Patents.*

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THOMAS F. MURPHY,  
*Assistant Commissioner of Patents.*